



Short communication

Carbon coated lithium sulfide particles for lithium battery cathodes

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H I G H L I G H T S

- Encapsulated lithium sulfide as cathode material for lithium sulfur batteries.
- Prevention of polysulfide dissolution by carbon encapsulation of lithium sulfide particles.
- High coulombic efficiencies (>99.5%) and stable cycling performance.

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In this paper, we investigated the properties of carbon coated lithium sulfide particles prepared following either a dry coating process or a wet coating process, using, respectively, sucrose or polyacrylonitrile (PAN) as carbon source. X-ray diffraction analysis revealed that the crystalline structure of the pristine Li₂S was basically preserved upon both coating processes. The dry coating process (Li₂S-C_{sucrose}) resulted in Li₂S particles covered only partially by smaller carbon particles, whereas the wet coating method (Li₂S-C_{PAN}) gave Li₂S particles, homogeneously decorated with thin carbon flakes. As a result, the cycling performance of Li₂S-C based electrodes was significantly improved, particularly for Li₂S-C_{PAN}, for which a coulombic efficiency of more than 99.5% was obtained.

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1. Introduction

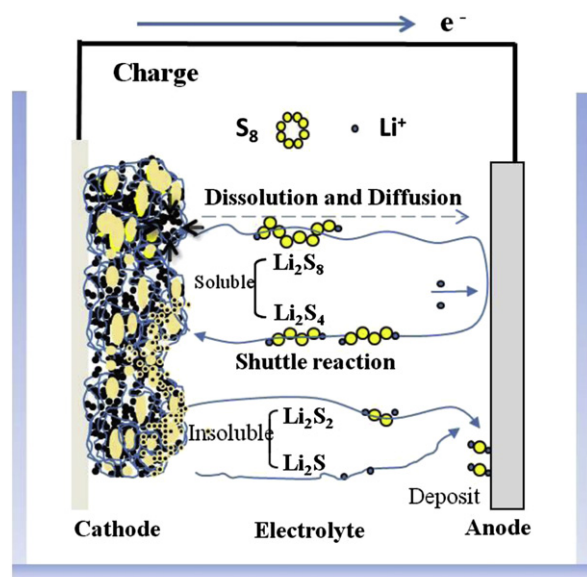
Sulfur is considered to be the most promising cathode material for the realization of *Next Generation* lithium batteries. Its high specific capacity (1672 mAh g⁻¹), ten times that of conventional lithium insertion cathodes, promises lithium batteries with a gravimetric energy density far exceeding the 500 Wh kg⁻¹ needed for the realization of electric vehicles and efficient stationary energy storage systems. Unlikely, present sulfur cathodes are affected by severe drawbacks, namely poor coulombic efficiency and active material loss, associated with the solubility of the intermediate discharge products, as seen in Fig. 1.

Polysulfide dissolution remains still the main hurdle preventing the development of lithium batteries with high gravimetric energy density. Its primary effect consists in reducing the coulombic efficiency of the cell and, thus, it can be easily identified comparing the charge and discharge capacities at a given cycle. So far, several attempts have been made to prevent the polysulfide dissolution by, for example, using gel-polymer electrolytes and solvent-free

polymer electrolytes [1–8], yet unsuccessfully. In fact, these attempts have resulted in limited cell capacity retention (about 75% upon 30 cycles) [7]. Other attempts have focused on trapping the sulfur active material in carbon porous structures or networks of carbon fibers and binders [3,6,9–30]. These approaches, however, suffered of the volumetric expansion of the cathode material upon discharge, which leads to its extrusion (or solubilization) out of the caging structure. Very recently [9], Nazar and coll. have reported excellent capacity performance for sulfur electrode supported on carbon nanospheres through a rather complex synthesis. Nevertheless, the coulombic efficiency is still an issue, especially considering that the electrodes were tested at relatively high currents, i.e., a short charging time. Combined approaches were also attempted. Novák and coll. [30] showed that the combination of polymer electrolytes and electrode binders allows the realization of Li/S cells with a good cycle life and interesting capacities. However, the coulombic efficiency of these cells was rather low (>87%) thus indicating that the polysulfide dissolution hurdle is still present.

The approach reported in here consists in encapsulating lithium sulfide particles (named Li₂S-C in the following) into a carbonaceous shell, which can then be used to realize composite electrodes for Li/S cell (Fig. 2). Moreover, the approach of using the end-

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$2\text{Li} + \text{S} \leftrightarrow \text{Li}_2\text{S}$ 1672 mAh/g-S overall reaction

$2\text{Li} + \text{S}_8 \leftrightarrow \text{Li}_2\text{S}_8$	209 mAh/g-S	step I	} Lithium polysulfide
$2\text{Li} + \text{Li}_2\text{S}_8 \leftrightarrow 2\text{Li}_2\text{S}_4$	209 mAh/g-S	step II	
$2\text{Li} + 2\text{Li}_2\text{S}_4 \leftrightarrow 4\text{Li}_2\text{S}_2$	418 mAh/g-S	step III	
$2\text{Li} + 4\text{Li}_2\text{S}_2 \leftrightarrow 8\text{Li}_2\text{S}$	836 mAh/g-S	step IV	Lithium sulfide

Fig. 1. Schematic illustration of the issues associated with the polysulfide solubility, namely, shuttle reaction (poor coulombic efficiency) and Li_2S deposition (active material loss). Lower panel: electrochemical redox processes taking place in a Li/S cell.

member of a fully discharged Li/S cell advantageously enables the replacement of metallic lithium by any kind of anode material currently used within lithium-ion battery technology. Furthermore, upon operation, the volume of the encapsulated particles never exceeds the initial volume thus ensuring the preservation of the encapsulating carbon shell. The obtained results indicate that the approach is viable to finally solve the polysulfide containment in next generation sulfur based batteries.

Here we demonstrate that carbon encapsulated lithium sulfide particles may be used for the realization of composite electrodes for Li/S cell, which show exceptionally high coulombic efficiency, practically close to 100%. Our proof-of-concept approach is based on the carbon encapsulation of the cathode material as depicted in Fig. 2. Although the use of lithium sulfide, rather than sulfur, for the realization of Li/S cells has been already proposed by Scrosati et al. [7], its encapsulation to prevent polysulfide dissolution has never been reported before. Carbon coating the low density, discharged product, Li_2S , rather than the more dense sulfur was the key to enable the mechanically stable encapsulation of this cathode material. Since only negative volume changes occur during the charge/discharge processes, no mechanical stress is applied on the encapsulating carbon, thus preventing the cracking of the shell and the subsequent release of soluble polysulfides into the electrolyte.

A key issue to solve, however, was to develop an effective coating procedure that did not affect the active material. Carbon coating of poorly conducting lithium intercalation materials has been already reported [31,32]. This approach, based on the use of an aqueous sucrose solution as the carbon source, has been successfully applied to enhance the electronic conductivity of several electrode materials [33–37]. However, Li_2S is very hygroscopic and reacts with water to form H_2S and Li_2O , thus making this approach not applicable. To avoid this inconvenient, we attempted a dry coating process (mechanical milling of Li_2S and sucrose) and a wet coating process (polyacrylonitrile, PAN, dissolved in N-methylpyrrolidone, NMP).

2. Experimental

2.1. Preparation of carbon encapsulated Li_2S

3 g of Li_2S (ABCR) were dispersed in 10 ml of acetonitrile (ALDRICH) and then ball-milled in a zirconia jar with 30 g of zirconia balls for 3 h to reduce the particle size. The Li_2S was collected by filtration and dried at 180 °C in vacuum (B-585, Buchi). Encapsulated Li_2S particles were synthesized starting from two different carbon sources, polyacrylonitrile (PAN) and sucrose. For the wet synthesis, 0.1 g of PAN was dissolved in 1 g of N-methylpyrrolidone (ALDRICH) at 20 °C. 1 g of Li_2S was dispersed by manual grinding in an agate mortar for 30 min. The composite was carbonized in argon atmosphere for 3 h after heating to 550 °C at a rate of 3 °C min⁻¹.

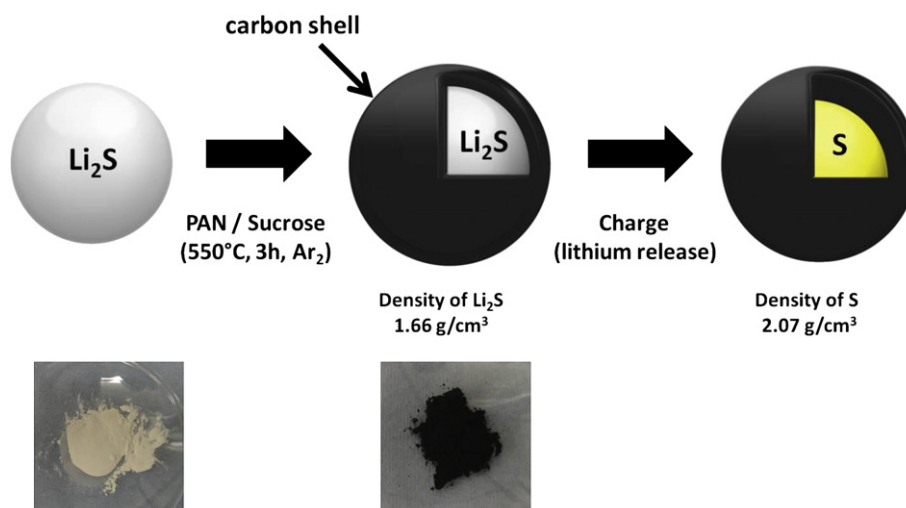


Fig. 2. Simplified schematic illustration of the carbon coated Li_2S synthesis and its volume change during the redox process (upper image). Images of the Li_2S powder prior and after the carbon coating process using polyacrylonitrile as carbon source (lower images). The change in color is indicative of the carbon coating. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The final composite material, $\text{Li}_2\text{S-C}$ was mechanically milled for 30 min to favor the dispersion of the coated particles. In the dry synthesis, sucrose was first manually ground in an agate mortar for half an hour to reduce its particle size. 1 g of Li_2S and 0.1 g of sucrose were mixed and manually ground in an agate mortar together for 30 min. The carbonization process was performed as described above.

2.2. Preparation of Li_2S electrodes

The encapsulated Li_2S powder was premixed with Super C65[®] (TIMCAL), in a 40:10 weight ratio. The dry powder was homogenized using planetary ball milling (Vario-Planetary Mill Pulverisette 4, Fritsch) at 400 rpm for 2 h. To this mixture, poly(vinylidene-fluoride)-(hexafluoropropylene) copolymer (PVdF-HFP Kynarflex 2801, Arkema) dissolved in N-methylpyrrolidone and additional Super C65[®] were added to prepare the electrode slurry. The slurry

was homogenized using planetary ball milling at 600 rpm for 3 h. A ball-to-powder ratio of 20:1 was employed using zirconia balls with a diameter of 5 mm in a zirconia jar of 80 ml full capacity. The slurry was casted on aluminum foil (SCHLENK) by using a laboratory doctor blade with a set wet film thickness of 100 μm . The slurry was dried for 12 h at 60 $^\circ\text{C}$ and further at 100 $^\circ\text{C}$ under vacuum for 10 h. The dry composition of the composite cathode was 40 wt.% $\text{Li}_2\text{S-C}$, 50 wt.% Super C65[®], and 10 wt.% PVdF-HFP. The cathode electrode was cut into circular disks of 1.13 cm^2 comprising ~ 2 mg of active mass loading.

2.3. Morphological and structural characterization

The XRD patterns of the three different samples in a 2θ range from 10 $^\circ$ to 90 $^\circ$ were collected on a D8-Advance powder X-ray diffractometer (BRUKER). The morphology of pristine and carbon coated Li_2S was investigated by means of SEM (ZEISS Auriga). The

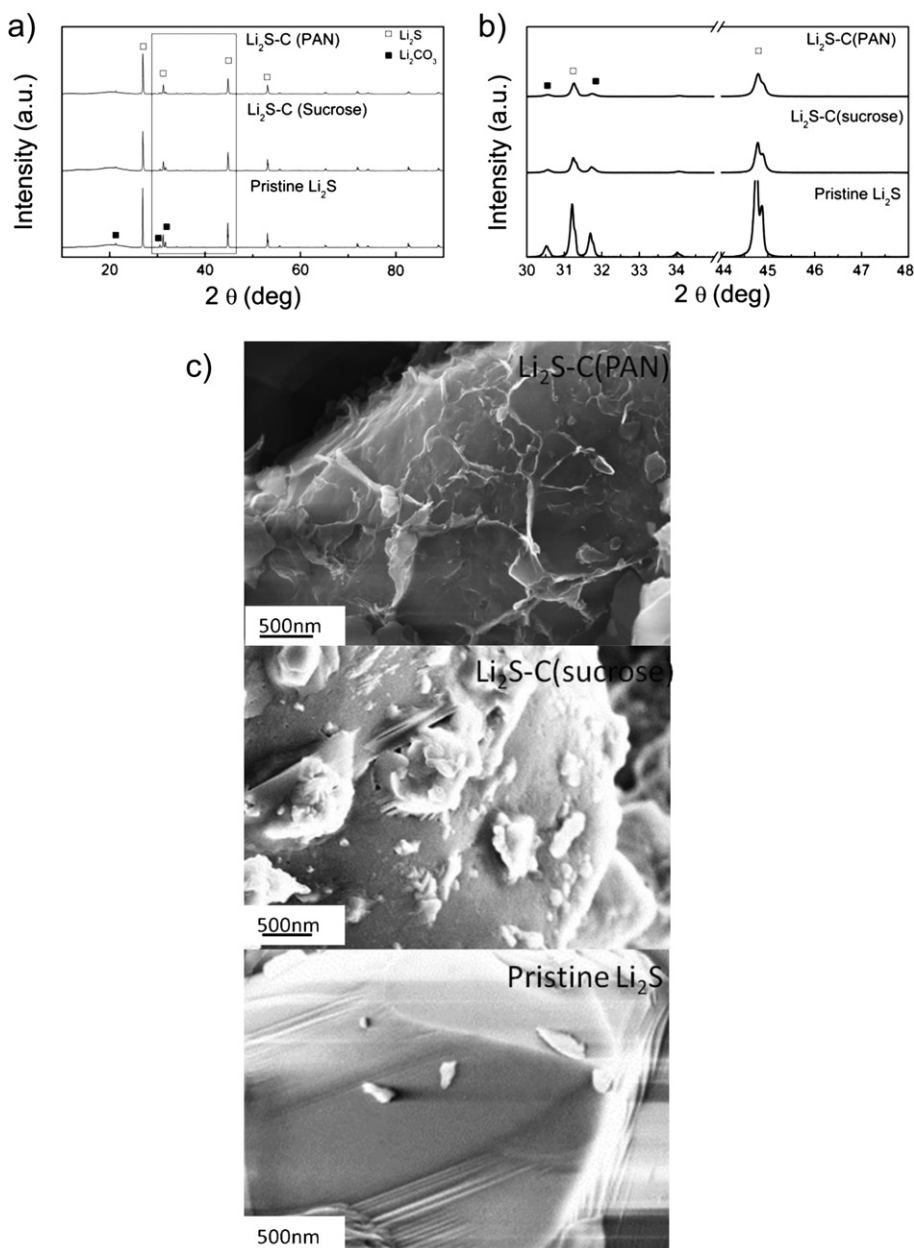


Fig. 3. a) X-ray diffraction patterns of Li_2S powder and carbon coated Li_2S . b) Magnification of the region marked by the rectangle in Fig. 3a. c) SEM images of pristine Li_2S (bottom) $\text{Li}_2\text{S-C}_{\text{sucrose}}$ (middle) and $\text{Li}_2\text{S-C}_{\text{PAN}}$ (top).

Table 1
Weight percent of elements in Li_2S and carbon coated Li_2S .

Sample	C (wt.%)	H (wt.%)	N (wt.%)	Carbon source	Method	Heat treatment
Li_2S	3.41	0.15	0.00			Dry vacuum 120 °C
$\text{Li}_2\text{S-C}_{\text{sucrose}}$	7.43	0.19	0.00	10 wt.% Sucrose	Dry mix	550 °C, 3 h, Ar
$\text{Li}_2\text{S-C}_{\text{PAN}}$	8.43	0.10	1.61	10 wt.% PAN	Wet mix	550 °C, 3 h, Ar
$\text{Li}_2\text{S-C}_{\text{PAN}}$	13.57	0.21	2.95	20 wt.% PAN	Wet mix	550 °C, 3 h, Ar

carbon content was determined by using an element analyzer (Elementar Vario EL III). Electrochemical studies were carried out in two electrode cells sealed in coffee bag-like envelopes. Metallic lithium (ROCKWOOD LITHIUM, battery grade) was used as the negative electrode. The cells were assembled by stacking the separator (CELGARD 2325, SP), containing liquid electrolyte, between the Li_2S cathode and the lithium metal anode in a dry room with a H_2O content of less than 0.5 ppm. The electrolyte was composed of a 0.5 M LiCF_3SO_3 solution in a 3:7 weight mixture of tetraethylene glycol dimethylether (TEGDME) and 1,3-dioxolan. The galvanostatic cycling tests were performed at room temperature in a voltage range from 1.2 V to 3.5 V at a constant current density of 23.33 mA g^{-1} , corresponding to a (dis-)charge rate of C/50 with respect to the theoretical specific capacity of Li_2S and approximately C/72 with respect to the theoretical specific capacity of sulfur, including the mass of Li_2CO_3 , which is present as an impurity, as well as the amount of carbon resulting from the applied carbon coating (MACCOR Battery Tester 4300).

3. Results and discussion

The effectiveness of the carbon coating is macroscopically evidenced by the change in color of the powder after the carbonization step (Fig. 2). Those black powders are insoluble in NMP. The X-ray diffractograms of pristine Li_2S are compared with those of the coated materials in Fig. 3. From the XRD patterns it is easily seen that both coating processes were successful in preserving basically the crystalline structure of Li_2S (JCPDS 77-2145, Fig. 3a). Exemplarily, no changes are observed in the position and the relative intensity of all XRD features including the minor reflections of Li_2S . However, a decreasing intensity of the obtained reflections accompanied by a slight broadening is observed, respectively decreasing and increasing in the order pristine Li_2S , $\text{Li}_2\text{S-C}_{\text{sucrose}}$, $\text{Li}_2\text{S-C}_{\text{PAN}}$ (Fig. 3b). Such a decrease in crystallinity is presumably related to the additional grinding ($\text{Li}_2\text{S-C}_{\text{sucrose}}$) and milling ($\text{Li}_2\text{S-C}_{\text{PAN}}$) steps performed for applying the carbon coating of the Li_2S particles. Apart from this, according to the reflections observed at 30.5° and 31.7° the presence of Li_2CO_3 (JCPDS 83-1454) as a second phase is indicated (Fig. 3a, black squared markers).

The SEM images (also shown in Fig. 3) clearly evidence the presence of carbonaceous deposit on the coated Li_2S particles. According to the elemental analysis (Table 1), pristine Li_2S before as well as after drying, contains 3.4 wt.% of carbon, which is from Li_2CO_3 (consequently around 16 wt.%) spontaneously formed by the reaction with humidity and CO_2 as confirmed by the XRD results (the commercial Li_2S material used was sealed in dry air). The elemental analysis results also indicate that the carbon content resulting from the encapsulation processing accounts to 4–5 wt.% of the total sample mass per % of carbon source material used. In coated $\text{Li}_2\text{S}_{\text{PAN}}$, in fact, the carbon content after pyrolysis increased twice as much when the PAN used in the processing was doubled (compare results in Table 1). However, the presence of hydrogen and nitrogen (the latter only for PAN) in the coating indicates that it contains not fully carbonized materials as a result of the relatively low carbonization temperature, which does not allow a full conversion of PAN to a pure carbon matrix structure [38,39]. However, the application

of higher temperatures would result in a degradation of the Li_2S crystalline structure.

In terms of homogeneity of the carbon coating, substantial differences are resulting from the two coating methods as observed by SEM analysis (Fig. 3c). The dry coating method (mechanical milling of Li_2S and sucrose) resulted in the formation of large carbon junks, which were only partially coating the Li_2S particle surface. On the other hand, the wet coating process led to the formation of a thin, flake-like carbonaceous film on the Li_2S particles, which offers a uniform coating of the active material particles. Nonetheless, it is important to notice that the morphology of this coating is far from being optimized. In fact, the carbon flakes appear to protrude partially from the particle surface, which involves a certain additional amount of carbon not needed for the particle coating. In addition, the carbon layer thickness, as seen from the flakes

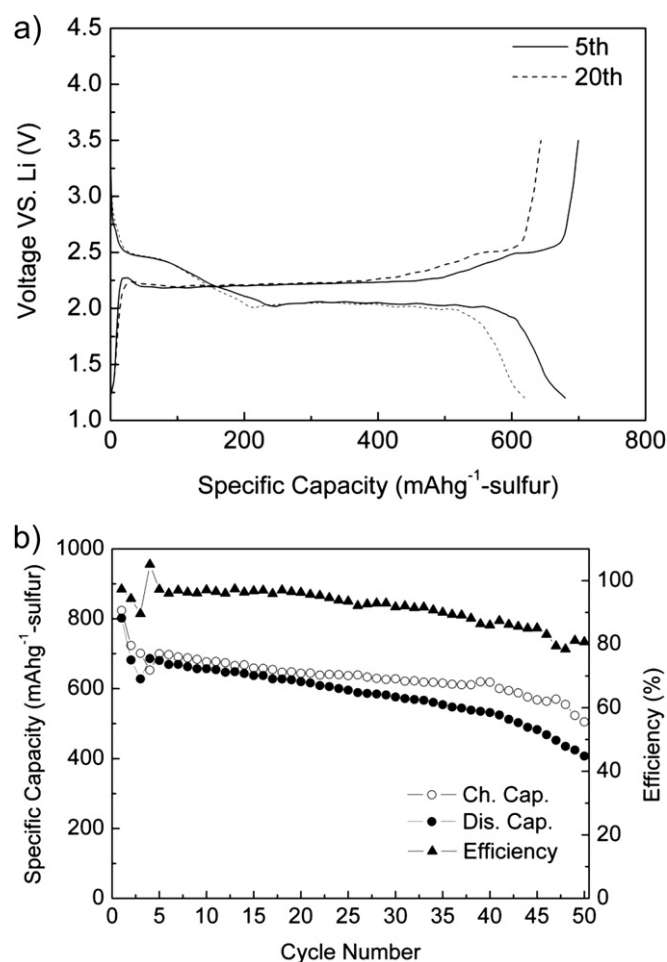


Fig. 4. Electrochemical performance of a $\text{Li}/\text{Li}_2\text{S-C}_{\text{sucrose}}$ cell subjected to continuous charge–discharge cycles at 23.33 mA g^{-1} (C/50 (Li_2S) or C/72 (sulfur)) in a voltage range extending from 1.2 V to 3.5 V (20 °C). a) Selected voltage profiles. b) Charge and discharge capacity and coulombic efficiency for the initial 50 cycles.

perpendicular to the Li_2S particle surface in the SEM picture of Fig. 3c, appears to be around at least several tens of nanometers, i.e., several times that of commercial lithium iron phosphate cathode powder [31]. Such a high thickness of carbon certainly results in a lower diffusivity of lithium through the particle shell.

The carbon-coated powders were used to prepare electrodes on aluminum foil substrates. The lower reactivity of the coated particles made this process facile and excellent electrode tapes were obtained. The electrochemical performance of such electrodes was verified by galvanostatic cycling. In the first step, an anodic current was applied to charge the cell, i.e., the cathode voltage was increased to favor the oxidation of Li_2S to sulfur while lithium ions were released into the electrolyte. In the following cathodic step, the sulfur was reduced and lithium ions were taken from the electrolyte to regenerate Li_2S . This latter process, which is spontaneous, corresponds to the discharge of the battery cell. In Fig. 4a) illustrates two selected voltage profiles recorded during the cycling test of an electrode containing $\text{Li}_2\text{S-C}_{\text{sucrose}}$ obtained via the dry carbon coating process. Although the shape of the voltage profiles does not substantially change upon cycling, a marked capacity decrease is observed, which can be even better observed in Fig. 4b). It is obvious that this capacity fading is strongly correlated to the coulombic efficiency of the cell, which significantly decreases after around 20 cycles, revealing that the polysulfide dissolution cannot be entirely prevented by the fragmented carbon coating offered by the dry coating process (see Fig. 3). However, electrodes based on

wet coated $\text{Li}_2\text{S-C}_{\text{PAN}}$ clearly show a dramatically improved coulombic efficiency of more than 99.5%, resulting in a significantly enhanced cycling stability (Fig. 5) and thus indicating that the concept of coating Li_2S particles by a homogenous carbon layer can successfully prevent polysulfide dissolution. Nevertheless, the obtained specific capacity for $\text{Li}_2\text{S-C}_{\text{PAN}}$ is slightly lower than that obtained for $\text{Li}_2\text{S-C}_{\text{sucrose}}$. This difference is related to the relatively lower carbon (and nitrogen) content in $\text{Li}_2\text{S-C}_{\text{sucrose}}$ rather than $\text{Li}_2\text{S-C}_{\text{PAN}}$ (Table 1), giving a factor of around 0.75 for the C + H + N ratio of the two different samples. As previously mentioned it is assumed that a lower carbon (and nitrogen) content – relatively to the particle size and thus the specific surface area – might have a beneficial influence on the overall electrochemical performance of carbon coated Li_2S particles and moreover result in an increased specific capacity of the final electrodes. Additionally, care will have to be taken to avoid any contact of the pristine Li_2S samples with air and humidity in order to avoid the presence of Li_2CO_3 phase impurities, which significantly reduces the achievable specific capacity.

4. Conclusions

Although it should be pointed out that the absolute capacity of the $\text{Li}_2\text{S-C}_{\text{PAN}}$ electrode is only three times that of LiCoO_2 , the most used material in present lithium-ion batteries, the results reported in this paper clearly indicate that the carbon coating of Li_2S is a viable strategy to solve the main hurdle preventing the development of high energy density lithium/sulfur batteries, namely the polysulfide dissolution. Nevertheless, the materials and the coating processes developed in this work are far from being optimized. Spherical Li_2S particles with diameter in the order of 1 μm (or lower) coupled with the formation of a thin and uniform carbon shell would substantially increase the capacity performance of carbon encapsulated Li_2S electrodes without affecting (if not improving) the exceptionally high resistance to polysulfide solubilization.

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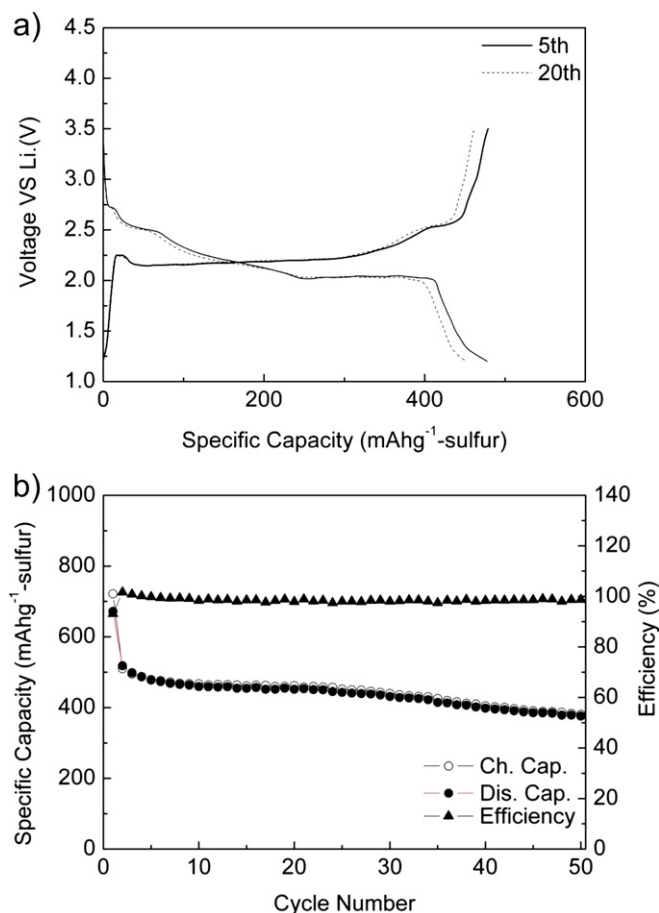


Fig. 5. Electrochemical performance of a $\text{Li/Li}_2\text{S-C}_{\text{PAN}}$ cell subjected to continuous charge–discharge cycles at 23.33 mA g^{-1} ($\text{C}/50$ (Li_2S) or $\text{C}/72$ (sulfur)) in the voltage range extending from 1.2 V to 3.5 V (20°C). a) Selected voltage profiles. b) Charge and discharge capacity and coulombic efficiency for the initial 50 cycles.

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